CHAPTER 6: DIFFUSION IN SOLIDS

Gear from case-hardened steel (C diffusion)

ISSUES TO ADDRESS...

- How does diffusion occur?
- Why is it an important part of processing?
- How can the rate of diffusion be predicted for some simple cases?
- How does diffusion depend on structure and temperature?

Diffusion- Steady and Non-Steady State

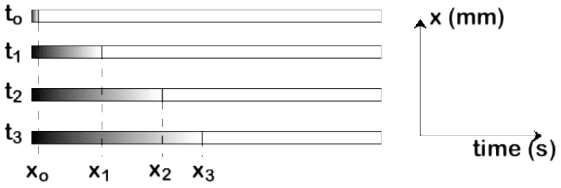
Diffusion - Mass transport by atomic motion

Mechanisms

- Gases & Liquids – random (Brownian) motion
- Solids – vacancy diffusion or interstitial diffusion

Simple Diffusion

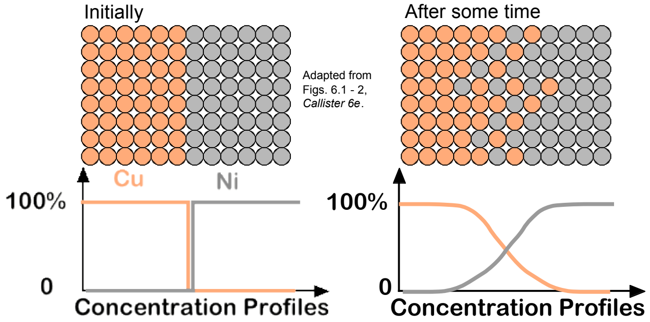
- Glass tube filled with water.
- At time t = 0, add some drops of ink to one end of the tube.
- Measure the diffusion distance, x, over some time.
- Compare the results with theory.



Inter-diffusion

- Interdiffusion: In alloys, atoms tend to migrate from regions of large concentration.

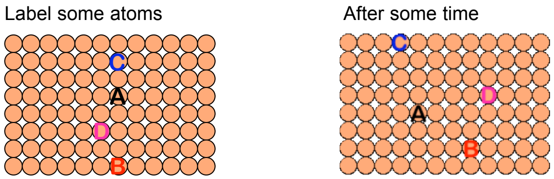
This is a diffusion couple.



Adapted from Figs. 6.1 - 2, *Callister 6e*.

Self-diffusion

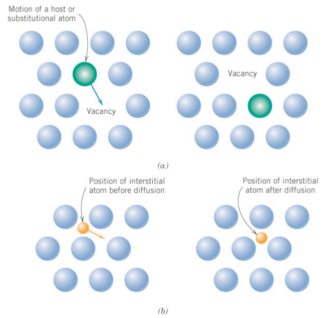
- Self-diffusion: In an elemental solid, atoms also migrate.


Label some atoms

After some time

Substitution-diffusion: vacancies and interstitials

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate* depends on (1) number of vacancies; (2) activation energy to exchange.



Number (or concentration*) **of Vacancies** at T

$$c_i = \frac{n_i}{N} = e^{-\frac{\Delta E}{k_B T}}$$

- $k_B T$ gives eV

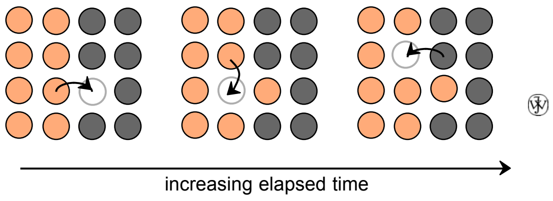
*** see web handout for derivation.**

ΔE is an activation energy for a particular process (in J/mol, cal/mol, eV/atom).

Substitution-diffusion

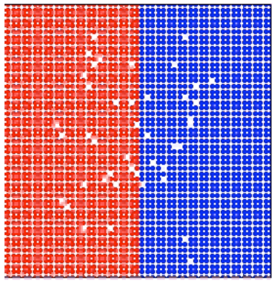
Vacancy Diffusion:

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate* depends on (1) number of vacancies;
  (2) activation energy to exchange.



Inter-diffusion across Interfaces

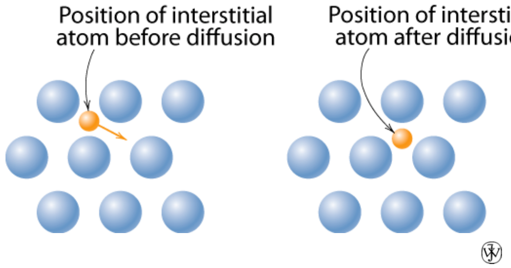
- Rate of substitutional diffusion depends on:
  - vacancy concentration
  - frequency of jumping.


(Courtesy P.M. Anderson)

Why should interstitial diffusion be faster than by vacancy mode of diffusion?

Diffusion Mechanisms

- Interstitial diffusion – smaller atoms diffuse between atoms.



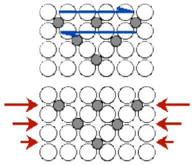
More rapid than vacancy diffusion

Processing using Diffusion

- Case Hardening:
  - -Diffuse carbon atoms into the host iron atoms at the surface.
  - -Example of interstitial diffusion is a case hardened gear.

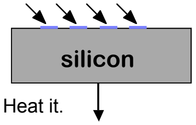
Fig. 6.0, *Callister 6e*. (courtesy of Surface Div., Midland-Ross.)

- Result: The "Case" is
  - -hard to deform: C atoms "lock" planes from shearing.
  - -hard to crack: C atoms put the surface in compression.

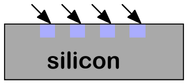


Processing using Diffusion

- Doping Silicon with P for n-type semiconductors:
- Process:
  1. Deposit P rich layers on surface.



  2. Heat it.
  3. Result: Doped semiconductor regions.



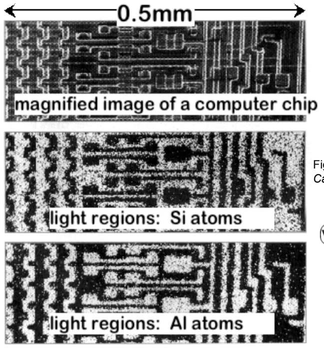


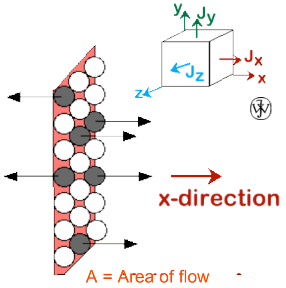
Fig. 18.0, *Callister 6e*.

Modeling rate of diffusion: flux

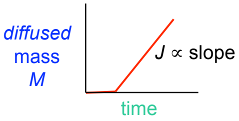
- Flux:

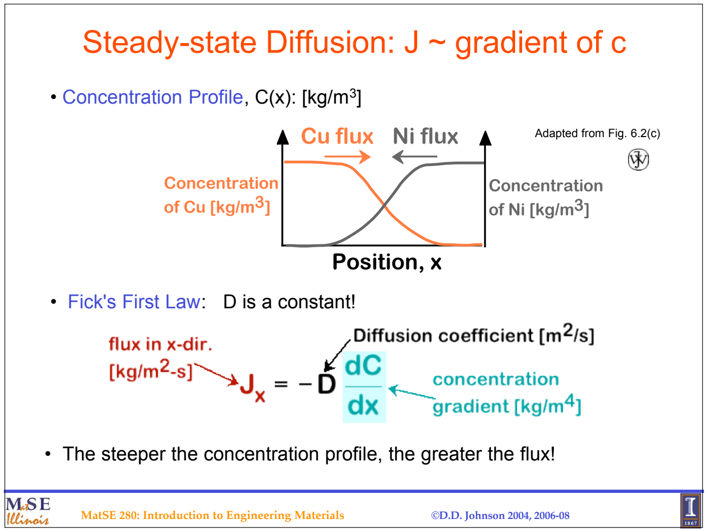
$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$

- Directional Quantity



- Flux can be measured for:
  - vacancies
  - host (A) atoms
  - impurity (B) atoms
- Empirically determined:
  - Make thin membrane of known surface area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane





Steady-state Diffusion: J ~ gradient of c

- Concentration Profile, C(x): [kg/m^3]

Adapted from Fig. 6.2(c)

- Fick's First Law: D is a constant!

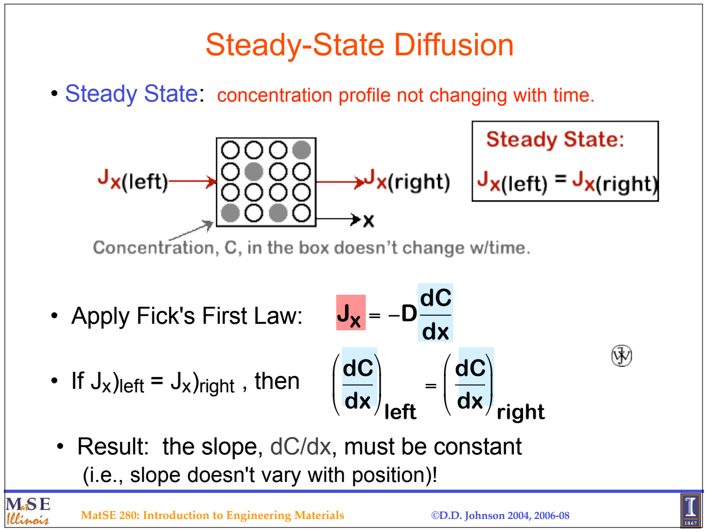
flux in x-dir. [kg/m^2-s]

$$J_x = -D\frac{dC}{dx}$$

Diffusion coefficient [m^2/s]

concentration gradient [kg/m^4]

- The steeper the concentration profile, the greater the flux!



Steady-State Diffusion

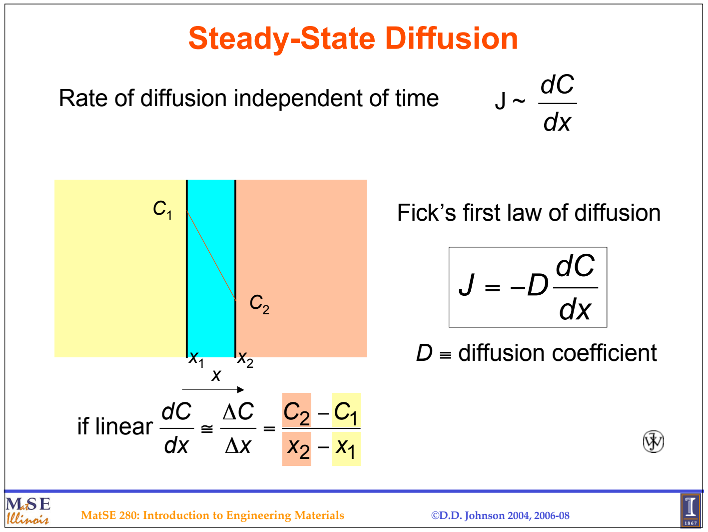
- Steady State: concentration profile not changing with time.

Concentration, C, in the box doesn't change w/time.

Steady State:

$J_x(\text{left}) = J_x(\text{right})$

- Apply Fick's First Law: $J_x = -D\frac{dC}{dx}$
- If $J_x)_{left} = J_x)_{right}$, then $\left(\frac{dC}{dx}\right)_{left} = \left(\frac{dC}{dx}\right)_{right}$
- Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!



Steady-State Diffusion

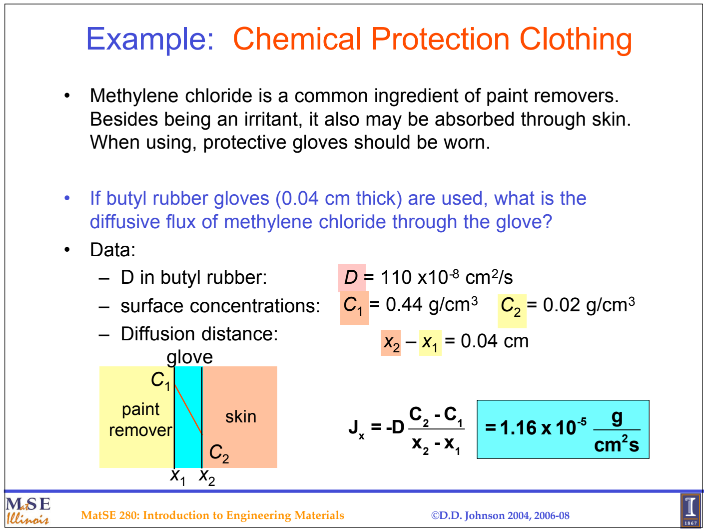
Rate of diffusion independent of time $J \sim \frac{dC}{dx}$

Fick's first law of diffusion

$$\boxed{J = -D\frac{dC}{dx}}$$

$D \equiv$ diffusion coefficient

if linear $\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}$



Example: Chemical Protection Clothing

- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using, protective gloves should be worn.
- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?
- Data:
  - D in butyl rubber: $D = 110 \times 10^{-8}$ cm^2/s
  - surface concentrations: $C_1 = 0.44$ g/cm^3 $C_2 = 0.02$ g/cm^3
  - Diffusion distance: $x_2 - x_1 = 0.04$ cm

$$J_x = -D\frac{C_2 - C_1}{x_2 - x_1} = 1.16 \times 10^{-5} \frac{\text{g}}{\text{cm}^2\text{s}}$$

Example: C Diffusion in steel plate

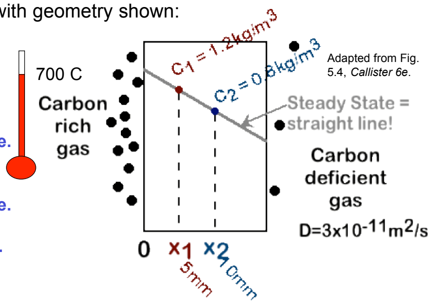
- Steel plate at 700⁰C with geometry shown:

Knowns:

C_1= 1.2 kg/m³ at 5mm (5 x 10⁻³ m) below surface.

C_2 = 0.8 kg/m³ at 10mm (1 x 10⁻² m) below surface.

D = 3 x10⁻¹¹ m²/s at 700 C.



Adapted from Fig. 5.4, *Callister 6e*.

- Q: In steady-state, how much carbon transfers from the rich to the deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9}\frac{kg}{m^2 s}$$

Example: Diffusion of radioactive atoms

- Surface of Ni plate at 1000⁰C contains 50% Ni^{63} (radioactive) and 50% Ni (non-radioactive).
- 4 microns below surface Ni^{63} /Ni = 48:52
- Lattice constant of Ni at 1000 C is 0.360 nm.
- Experiment shows that self-diffusion of Ni is 1.6 x 10⁻⁹ cm²/sec

What is the flux of Ni^{63} atoms through a plane 2 μm below surface?

$$C_1 = \frac{(4Ni/cell)(0.5Ni^{63}/Ni)}{(0.36x10^{-9}m)^3/cell} = 42.87x10^{27}Ni^{63}/m^3 \qquad C_2 = \frac{(4Ni/cell)(0.48Ni^{63}/Ni)}{(0.36x10^{-9}m)^3/cell} = 41.15x10^{27}Ni^{63}/m^3$$

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = -(1.6x10^{-13}m^2/sec)\frac{(41.15-42.87)x10^{27}Ni^{63}/m^3}{(4-0)x10^{-6}m} = +0.69x10^{20}Ni^{63}/m^2 \bullet s$$

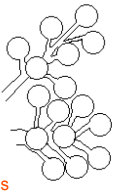
How many Ni^{63} atoms/second through cell? $J \bullet (0.36nm)^2 = 9\ Ni^{63}/s$

Where can we use Fick's Law?

Fick's law is commonly used to model transport processes in

- foods,
- clothing,
- biopolymers,
- pharmaceuticals,
- porous soils,
- semiconductor doping process, etc.

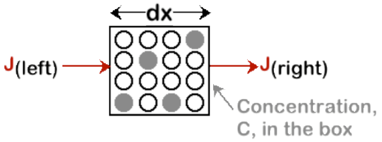
Example
The total membrane surface area in the lungs (alveoli) may be on the order of **100 square meters** and have a thickness of less than a **millionth of a meter**, so it is a very effective **gas-exchange interface**.



CO_2 in air has D~16 mm²/s, and, in water, D~ 0.0016 mm²/s

Non-Steady-State Diffusion

- Concentration profile, C(x), changes w/ time.



- To conserve matter:

$$\boxed{\frac{J(right) - J(left)}{dx}} = -\frac{dC}{dt}$$

$$\boxed{\frac{dJ}{dx}} = -\frac{dC}{dt}$$

- Fick's First Law:

$$J = -D\frac{dC}{dx} \quad \text{or}$$

$$\boxed{\frac{dJ}{dx}} = -D\frac{d^2C}{dx^2} \quad \text{(if D does not vary with x)}$$

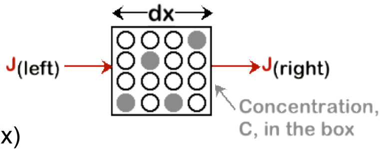
equate

- Governing Eqn.:

$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

Non-Steady-State Diffusion: another look

- Concentration profile, C(x), changes w/ time.



- Rate of accumulation C(x)

$$\frac{\partial C}{\partial t}dx = J_x - J_{x+dx} \quad \rightarrow \quad \frac{\partial C}{\partial t}dx = J_x - (J_x + \frac{\partial J_x}{\partial x}dx) = -\frac{\partial J_x}{\partial x}dx$$

- Using Fick's Law: $\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x} = -\frac{\partial}{\partial x}\left(-D\frac{\partial C}{\partial x}\right)$ Fick's 2nd Law

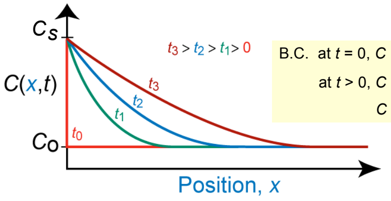
- If D is constant: Fick's Second "Law" $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \approx \left(D\frac{\partial c^2}{\partial x^2}\right)$

Non-Steady-State Diffusion: C = c(x,t)

concentration of diffusing species is a function of both time and position

Fick's Second "Law" $\frac{\partial c}{\partial t} \approx \left(D\frac{\partial c^2}{\partial x^2}\right)$

- **Copper diffuses into a bar of aluminum.**



B.C. at $t = 0$, $C = C_o$ for $0 \le x \le \infty$

at $t > 0$, $C = C_S$ for $x = 0$ (fixed surface conc.)

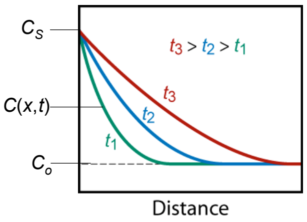
$C = C_o$ for $x = \infty$

Adapted from Fig. 6.5, *Callister & Rethwisch 3e*.

Non-Steady-State Diffusion

- Cu diffuses into a bar of Al.

Fick's Second "Law": $\frac{\partial c}{\partial t} \approx \left(D\frac{\partial c^2}{\partial x^2}\right)$



- Solution: $\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

"error function" Values calibrated in Table 6.1

$$erf(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$$

Example: Non-Steady-State Diffusion

FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface C content at 1.0 wt%.

If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, what temperature was treatment done?

Solution

$$\frac{C(x,t) - C_o}{C_s - C_o} = \frac{0.35 - 0.20}{1.0 - 0.20} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - \text{erf}(z) \quad \therefore \text{erf}(z) = 0.8125$$

Using Table 6.1 find z where erf(z) = 0.8125. Use interpolation.

z	erf(z)
0.90	0.7970
z	0.8125
0.95	0.8209

$$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

So, $z = 0.93$

Now solve for *D* $z = \frac{x}{2\sqrt{Dt}} \Rightarrow D = \frac{x^2}{4z^2t}$

$$\therefore D = \left(\frac{x^2}{4z^2t}\right) = \frac{(4 \text{ x } 10^{-3}\text{m})^2}{(4)(0.93)^2(49.5\text{ h})}\frac{1\text{ h}}{3600\text{ s}} = 2.6 \text{ x } 10^{-11}\text{ m}^2/\text{s}$$

Solution (cont.):

- To solve for the temperature at which D has the above value, we use a rearranged form of Equation (6.9a);

$D=D_0 \exp(-Q_d/RT)$

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

- From Table 6.2, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}$ m²/s Q_d = 148,000 J/mol $D = 2.6 \times 10^{-11}$ m²/s

$$\therefore \quad T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3\text{x}10^{-5} \text{ m}^2/\text{s} - \ln 2.6\text{x}10^{-11} \text{ m}^2/\text{s})}$$

T = 1300 K = 1027°C

Example: Processing

- Copper diffuses into a bar of aluminum.
- 10 hours processed at 600 C gives desired C(x).
- How many hours needed to get the same C(x) at 500 C?

Key point 1: $C(x,t_{500C}) = C(x,t_{600C})$.
Key point 2: Both cases have the same C_o and C_s.

- Result: Dt should be held constant.

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \longrightarrow (Dt)_{500°C} = (Dt)_{600°C}$$

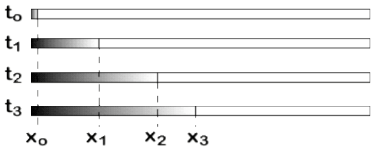
- Answer:

$$t_{500} = \frac{(\overset{5.3\text{x}10^{-13}\text{m}^2/\text{s}}{D}\overset{10\text{hrs}}{t})_{600}}{\underset{4.8\text{x}10^{-14}\text{m}^2/\text{s}}{D}_{500}} = 110\text{hr}$$

Note
D(T) are T dependent!
Values of D are provided.

Diffusion Analysis

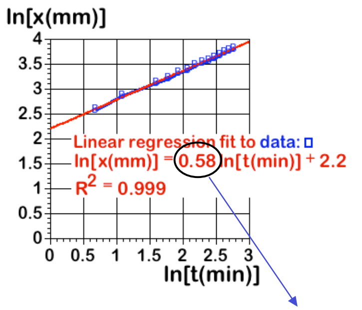
- The experiment: we recorded combinations of t and x that kept C constant.



$$\frac{C(x_i,t_i) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x_i}{2\sqrt{Dt_i}}\right) = \text{(constant here)}$$

- Diffusion depth given by: $x_i \propto \sqrt{Dt_i}$

Data from Diffusion Analysis



- Experimental result: $x \sim t^{0.58}$
- Theory predicts $x \sim t^{0.50}$ from $x_i \propto \sqrt{Dt_i}$
- Close agreement.

Diffusion and Temperature

- Diffusivity increases with T exponentially (so does Vacancy conc.).

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

D = diffusion coefficient [m²/s]

D_o = pre-exponential [m²/s] (see Table 6.2)

Q_d = activation energy [J/mol or eV/atom]

R = gas constant [8.314 J/mol-K]

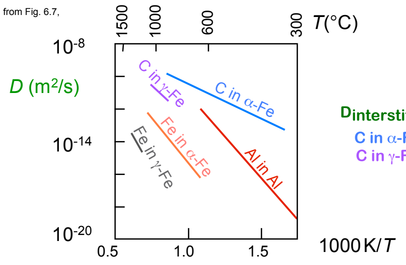
T = absolute temperature [K]

Note: $\ln D = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right)$ $\log D = \log D_0 - \frac{Q_d}{\mathbf{2.3}R}\left(\frac{1}{T}\right)$

Diffusion and Temperature

- Experimental Data:

Adapted from Fig. 6.7,



$D_{interstitial}$ >> $D_{substitutional}$

C in α-Fe
C in γ-Fe

Cu in Cu
Al in Al
Fe in α-Fe
Fe in γ-Fe
Zn in Cu

Adapted from Fig. 6.7, *Callister & Rethwisch 3e*.
(Data for Fig. 6.7 from E.A. Brandes and G.B. Brook (Ed.) *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, 1992.)

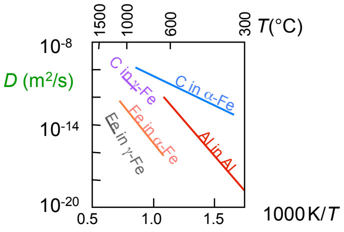
Example: Comparing Diffuse in Fe

Is C in fcc Fe diffusing faster than C in bcc Fe?

(Table 6.2)

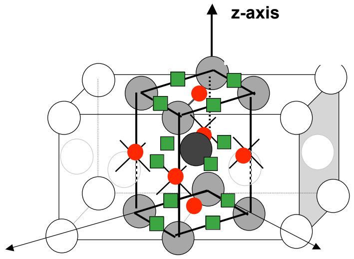
- fcc-Fe: D_0=2.3x10⁻⁵(m²/2)
  Q=1.53 eV/atom
  T = 900 C D=5.9x10⁻¹²(m²/2)

- bcc-Fe: D_0=6.2x10⁻⁷(m²/2)
  Q=0.83 eV/atom
  T = 900 C D=1.7x10⁻¹⁰(m²/2)



- FCC Fe has both higher activation energy Q and D_0 (holes larger in FCC).
- BCC and FCC phase exist over limited range of T (at varying %C).
- Hence, at same T, BCC diffuses faster due to lower Q.
- Cannot always have the phase that you want at the %C and T you want!
  which is why this is all important.

Connecting Holes, Diffusion, and Stress



Red **octahedral fcc**
Green + Red **octahedral bcc**

FCC represented as a BCT cell, with relevant holes.

Other Types of Diffusion (Beside Atomic)

- **Flux is general concept: e.g. charges, phonons,…**
- Charge Flux – $j_q = \frac{1}{A}\frac{dq}{dt} = \frac{1}{A}\frac{d(Ne)}{dt}$

e = electric chg.
N = net # e- cross A

Defining conductivity σ
(a material property)
$j = -\sigma \frac{dV}{dx}$

Solution: Fick's 2nd Law
$$\frac{V_x - V_s}{V_0 - V_s} = erf\left(\frac{x}{2\sqrt{\sigma t}}\right)$$

Ohm's Law $j_q = \frac{I}{A} = \frac{1}{A}\frac{V}{R} = \sigma\frac{V}{\ell}$

- Heat Flux –
  (by phonons)
  $Q = \frac{1}{A}\frac{dH}{dt} = \frac{1}{A}\frac{d(N\varepsilon)}{dt}$

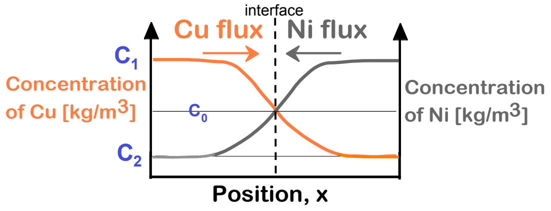
N = # of phonons with
avg. energy ε

Defining thermal conductivity κ
(a material property)
$Q = -\kappa \frac{dT}{dx}$

Solution: Fick's 2nd Law
$$\frac{T_x - T_s}{T_0 - T_s} = erf\left(\frac{x}{2\sqrt{ht}}\right)$$

Or w/ Thermal Diffusivity: $h = \frac{\kappa}{c_V \rho}$ $Q = c_V \rho T$

Inter-diffusion (diffusion couples)

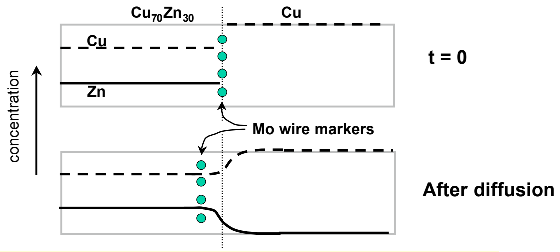


Assuming $D_A = D_B$: $\frac{C_1^x - C_0}{C_1 - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$ $C_0 = (C_1+C_2)/2$

$For\ C_2^x$ **Curve is symmetric about C_0,** $erf(-z) = -erf(z)$

Kirkendall Effect: What is $D_A > D_B$?

- Kirkendall studied Mo markers in Cu-brass (i.e., fcc $Cu_{70}Zn_{30}$).
- Symmetry is lost: Zn atoms move more readily in one direction (to the right) than Cu atoms move in the other (to the left).

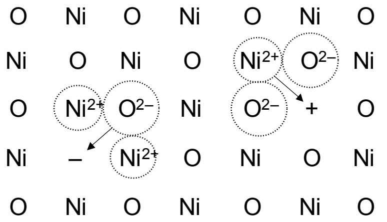


- When diffusion is asymmetric, interface moves away markers, i.e., there is a net flow of atoms to the right past the markers.
- Analyzing movement of markers determines D_{Zn} and D_{Cu}.
- Kirkendall effect driven by vacancies, effective for T > 0.5 T_{melt}.

Diffusion in Compounds: Ionic Conductors

- **Unlike diffusion in metals, diffusion in compounds involves second-neighbor migration.**
- **Since the activation energies are high, the D's are low unless vacancies are present from *non-stoichiometric ratios* of atoms.**

e.g., NiO
There are
Schottky defects



- **The two vacancies cannot accept neighbors because they have wrong charge, and ion diffusion needs 2nd neighbors with high barriers (activation energies).**

Diffusion in Compounds: Ionic Conductors

- D's in an ionic compound are seldom comparable because of size, change and/or structural differences.
- Two sources of conduction: ion diffusion and via e⁻ hopping from ions of variable valency, e.g., Fe^{2+} to Fe^{3+}, in applied electric field.

e.g., ionic

- In NaCl at 1000 K, $D_{Na+} \sim 5D_{Cl-}$,whereas at 825 K $D_{Na+} \sim 50D_{Cl-}$!
- This is primarily due to size r_{Na+} = 1 A vs r_{Cl-}=1.8 A.

e.g., oxides

- In uranium oxide, $U^{4+}(O^{2-})_2$, at 1000 K (extrapolated), $D_O \sim 10^7\ D_U$.
- This is mostly due to charge, i.e. more energy to activate 4+ U ion.
- Also, UO is not stoichiometric, having U^{3+} ions to give UO_{2-x}, so that the anion vacancies significantly increase O^{2-} mobility.

e.g., solid-solutions of oxides (leads to defects, e.g., vacancies)

- If $Fe_{1-x}O$ (x=2.5-4% at 1500 K, $3Fe^{2+}$ -> $2Fe^{3+}$ + vac.) is dissolved in MgO under reducing conditions, then Mg^{2+} diffusion increases.
- If MgF_2 is dissolved in LiF ($2Li^+$ -> Mg^{2+} + vac.), then Li^+ diffusion increases. All due to additional vacancies.

Ionic Conduction: related to fuel cells

- Molten salts and aqueous electrolytes conduct charge when placed in electric field, +q and –q move in opposite directions.
- The same occurs in solids although at much slower rate.
  - Each ion has charge of Ze (e = 1.6 x 10^{-19} amp*sec), so ion movement induces ionic conduction
  - Conductivity $\sigma = n\mu Ze$ is related to mobility, μ, which is related to D via the Einstein equations: $\mu = ZeD / k_BT$
  - Hence

$$\sigma_{ionic} = \frac{nZ^2e^2}{k_BT} D = \frac{nZ^2e^2}{k_BT} D_o e^{-Q/RT}$$

$$\log_{10} \sigma_{ionic} \sim \ln\left(\frac{nZ^2e^2}{k_BT} D_o\right) - \frac{Q}{2.3RT}$$

So, electrical conduction can be used determine diffusion data in ionic solids.

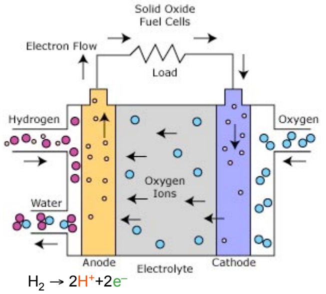
e.g., What conductivity results by Ca^{2+} diffusion in CaO at 2000 K?

- **CaO has NaCl structure with a= 4.81 A, with D(2000 K)~10^{-14}m^2/s, and Z=2.**

$$n_{Ca^{2+}} = \frac{4}{cell} \frac{cell}{(4.81x10^{-10} m)^3} = 3.59x10^{28} / m^3$$

$$\sigma = \frac{nZ^2e^2}{k_BT} D \sim \frac{1.3x10^{-5}}{ohm - cm}$$

Example: solid-oxide fuel cell (SOFC)



$H_2 \rightarrow 2H^+ + 2e^-$

$O^{2-} + 2H^+ + 2e^- \rightarrow H_2O$

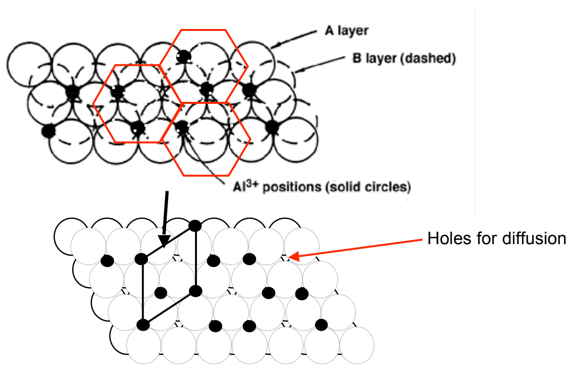
Image: http://www.ip3.unipg.it/FuelCells/en/htfc.asp

- SOFC is made up of four layers, three of which are ceramics (hence the name).
- A single cell consisting of these four layers stacked together is only a few mm thick.
- Need to stack many, many together to have larger DC current.

Overall: $H_2 + 1/2O_2 \rightarrow H_2O$

S. Haile's SOFC (2004 best): Thin-film of Sm-doped Ceria electrolyte (CeO_2, i.e. $Sm_xCe_{1-x}O_{2-x/2}$) and BSCF cathode (Perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$) show high power densities – over 1 W/cm² at 600 C – with humidified H_2 as the fuel and air at the cathode.

Ceramic Compounds: Al_2O_3



Unit cell defined by Al ions: 2 Al + 3 O

Summary: Structure and Diffusion

Diffusion FASTER for...	Diffusion SLOWER for...
open crystal structures	close-packed structures
lower melting T materials	higher melting T materials
materials w/secondary bonding	materials w/covalent bonding
smaller diffusing atoms	larger diffusing atoms
cations	anions
lower density materials	higher density materials